

Earliest traces of life – distinguishing techniques and present status of search.

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The oldest carbon containing sedimentary rocks currently known are found in the Isua Supracrustal Belt (ISB) dated at 3.78 billion years. Much attention has been focused on beds of iron carbonate in the ISB containing isotopically fractionated graphite, suggested to be remnants of early life forms in what was thought to be a shallow water sedimentary carbonate. Our recent work has however shown this rock to be a late metasomatic deposit formed at high temperature deep in the crust, and the graphite to have formed by disproportionation of the ferrous carbonate into magnetite and graphite. The discovery that this process leads to fractionation into a range of carbon isotope compositions calls for caution in indiscriminate reliance on isotopic evidence for biogenic carbon in metamorphic rocks.

Another potential source of error arises from often miniscule amounts of organic contamination that in rocks with an exceedingly low total carbon content, such as the ISB banded iron formation, may dominate the analytical yield of carbon and nitrogen. Removal of this complication requires analysis by stepwise heating.

These considerations leave one specific formation in the ISB as the currently most promising source of biogenic carbon – the carbonaceous black shale. The abundant carbon particles here show a wide range of isotopic ratios with $\delta^{13}\text{C}$ -26 as negative extreme. The lack of ferrous carbonate and magnetite as well as of other metasomatic features seem to eliminate disproportionation as a source of carbon and carbon isotope fractionation in this formation. After dissolution of the main components of the rock in hydrofluoric acid, a relatively low nitrogen content - of the order of 10 ppm - is found in the carbonaceous residue. The structure of the carbon, thought to be a significant discriminating feature, is as yet unknown.

The organization of macromolecular units is of diagnostic value in recognizing metamorphosed biogenic carbon (kerogen). In contrast to graphite, such carbon contains both five- and six membered rings forcing the otherwise planar molecular carbon sheets, to pucker and to aggregate into curved units. All occurrences of Proterozoic and Archean kerogens investigated by high resolution transmission electron microscopy in the seminal work by Buseck and collaborators show these features. A single carbon sample, from the ISB, was found to display dominantly planar molecular sheets and was quoted as an example of the ultimate conversion of kerogen to graphite. There are reasons to believe, however, that this is a sample of carbon from the Isua metacarbonate that we found to be an inorganic precipitate formed by disproportionation and to display the electron diffraction features of crystalline graphite.